No. 1

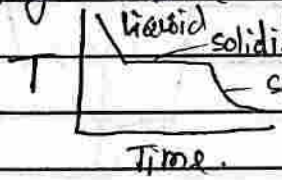
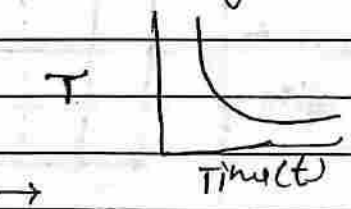
Date

Solid state

State of matter which has fixed shape, size and volume is called solid state.

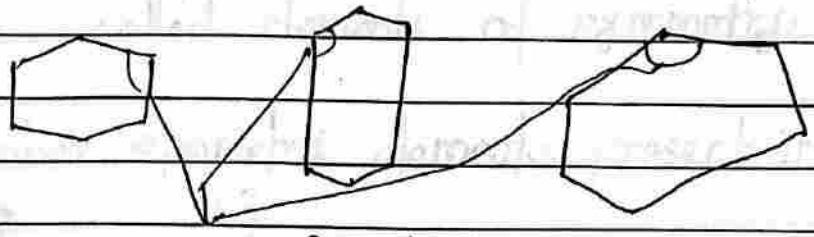
Solid state chemistry is concerned with the synthesis, structure, properties and applications of solid materials. The materials are usually inorganic, but not exclusively so.

Solids are of two types.

Crystalline	Amorphous
→ Solid in which constituent particles are arranged in regular fashion.	→ Solid in which constituent particles are not arranged in regular fashion.
→ They have definite geometric shape	→ They have irregular shapes.
→ They have sharp melting points.	→ They have a range of melting point.
→ They are anisotropic	→ They are isotropic.
→ They have a clean cleavage.	→ They undergo an irregular cut.
→ They have definite heat of fusion.	→ They do not have definite heat of fusion.
→ They do not have smooth cooling curve. 	→ They have smooth cooling curve. 
→ They are true solids e.g. NaCl, sugar, metal etc. Quartz (Crystalline SiO_2)	→ They are supercooled liquids or pseudosolids. e.g. glass, SiO_2, rubber etc

Interfacial Angles: In a crystal the angle between two faces is called interfacial angle.

e.g.



Interfacial angle.

- Interfacial angle of a crystal remain same throughout irrespective of the condition.

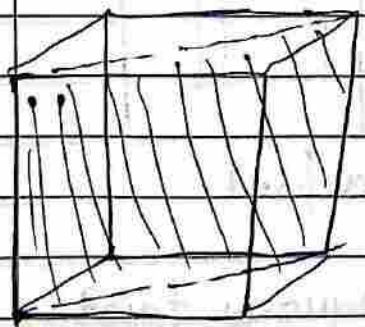
Symmetry: means that a certain portion of an object looks exactly like another portion of the same object.

Symmetry in Crystal Systems.

3 types

Plane

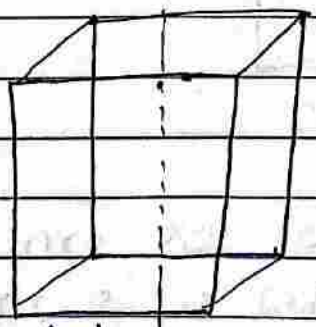
When an imaginary plane can divide a crystal into two parts such that one is the exact mirror image of the other



Axis

When crystal is rotated by 360°, if the same appearance is observed then crystal is said to have axis of symmetry

C_4

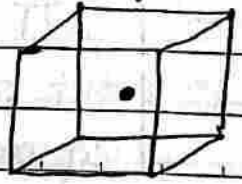


4-fold axis

Centre

Centre of symmetry is such a point that any line drawn through it intersects the surface of the crystal at equal distances in both directions.

→ A crystal have only one plane of symmetry.



Elements of Symmetry of a crystal:

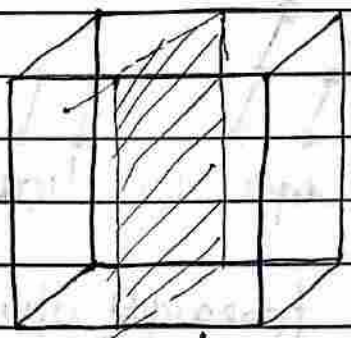
Total number of symmetry elements present in a crystal is called elements of symmetry.

Total number symmetry elements present in a cubic crystal ⇒ 23

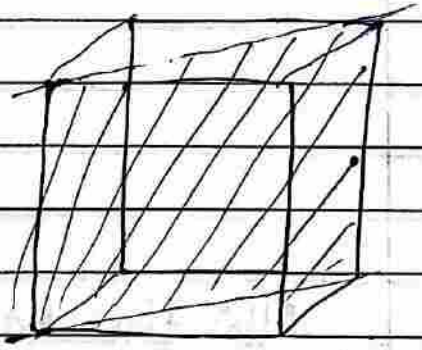
- Point: 1
- Plane: 9
  - 3 Rectangular
  - 6 Diagonal
- Axis: 13
  - C-4: 3
  - C-3: 4
  - C-2: 6

Plane of Symmetry

- Rectangular Plane
- Diagonal Plane.



Rectangular

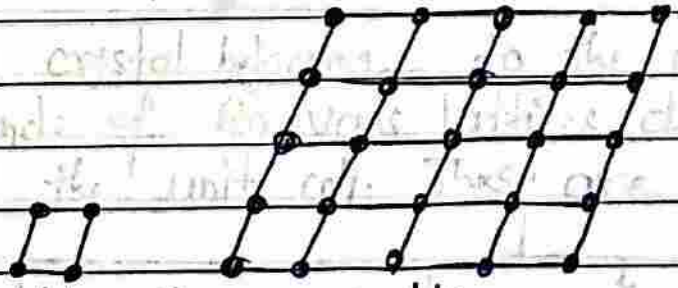


Diagonal Plane.

Point Groups: There are 32 combinations of symmetry elements of a crystal. These are called 32 point groups. There are seven types of crystal system which forms 32 point groups.

Crystal Systems:
Cubic or regular
Tetragonal
Orthorhombic
Monoclinic
Hexagonal
Rhombohedral or trigonal
Triclinic

Space Lattice and unit Cell:
The particles in crystals are arranged in regular patterns that extend in all directions. The overall arrangement of particles in a crystal is called the crystal lattice, space lattice or simply lattice.
To describe the structure of a crystal it is convenient to view it as being made of a large number of basic units. The simple basic unit or the building block of the crystal lattice is called the unit cell.



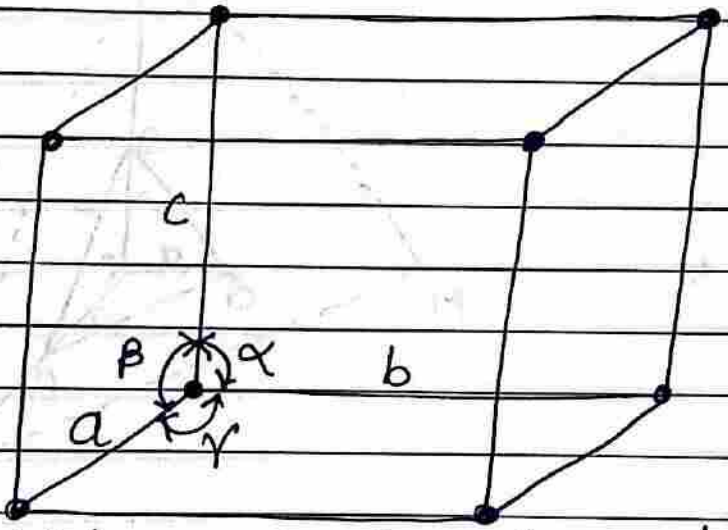
unit cell Space Lattice

How to Represent Crystal Lattice and unit Cell:
The crystal lattice of a substance is depicted by showing the position of particles in space. These positions are represented by bold dots or circles and are referred to as lattice points or lattice sites.
The overall shape and structure of a crystal system is governed by that of the unit cell of which it is composed.

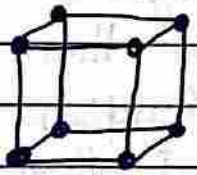
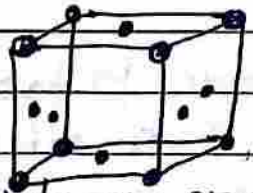
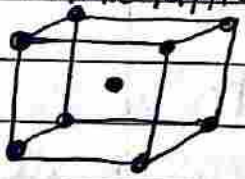
Parameters of the Unit Cells:

In 1850, August Bravais, a French mathematician observed that the crystal lattice of a substances may be categorised into seven types. These are called Bravais lattices and the corresponding unit cells are reffered to as Bravais unit cells. The unit cells may be categorised by the following parameters:

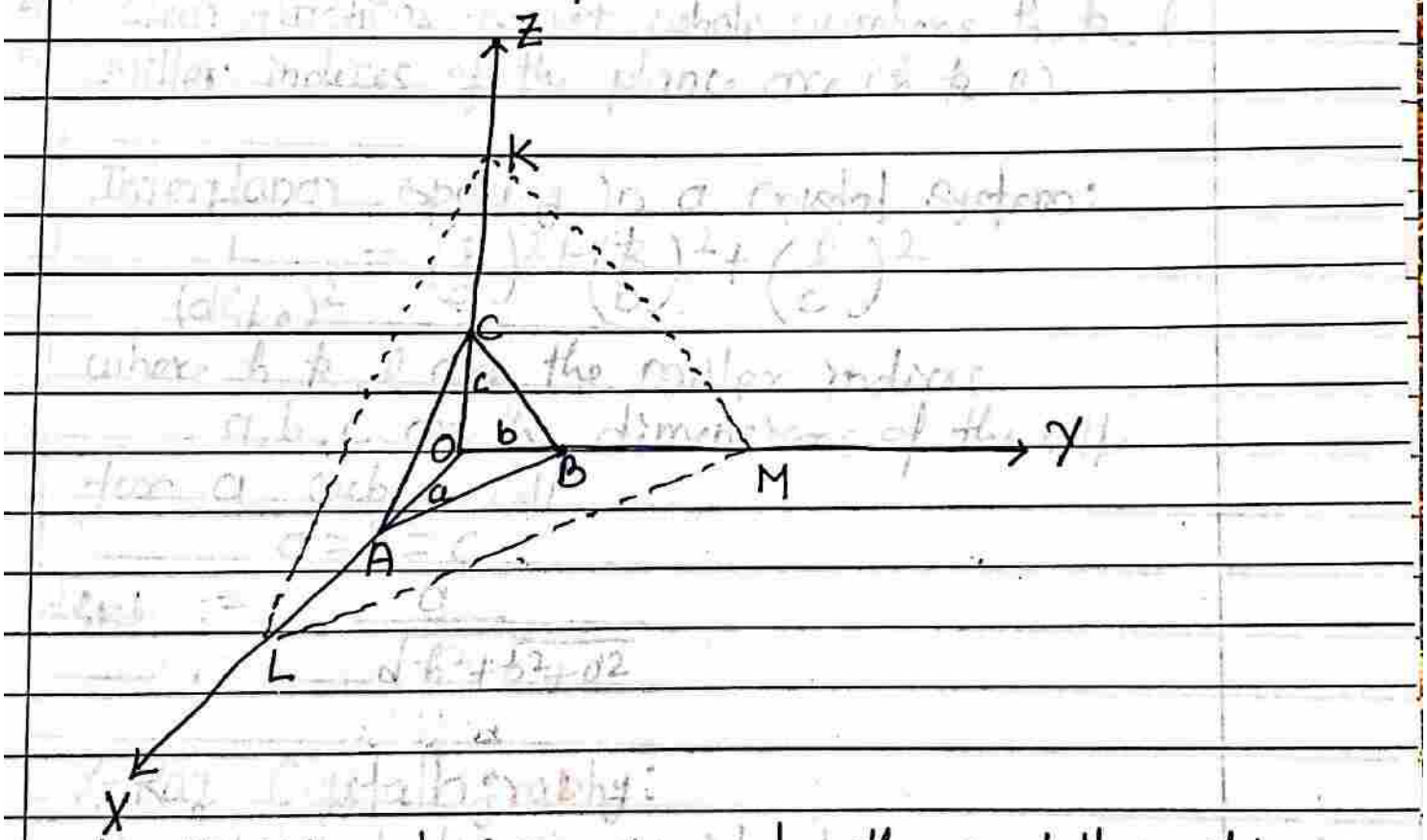
i) relative lengths of the edges along the three axes (a, b, c).
ii) the three angles between the edges (α, β, γ)



The crystal belonging to the cubic system have 3 kinds of Bravais lattices depending upon the shape of the unit cell. These are.

Simple or Primitive Cubic lattice (P)	Face centered cubic lattice (F)	Body centered cubic lattice (I)
		
Points present only at the corners of unit cell	Points are present at all corners and all six faces	Points present at the corners and body of the cube.

Law of Rational Indices: This law states that the intercepts of any face of a crystal along the crystallographic axes are either to the unit intercepts (a, b, c) or some simple whole number multiples of them. e.g. na, n'b, n''c etc. where n, n', n'' etc are simple whole numbers.



Let OX, OY and OZ represents the crystallographic axes and let ABC be a unit plane. The unit intercepts will then be a, b and c. According to above law, the intercepts of any face such as KLM, on the same three axes will be simple whole number multiples of a, b and c respectively.

Miller Indices: are a set of integers (h, k, l) which are used to describe a given plane in a crystal. The miller indices of a face of a crystal are inversely proportional to the intercepts of that face on the various axes.

How to Find Miller Indices?

Rule:

1. Prepare a 3-column table with the unit cell axes at the tops of the columns.
2. Enter in each column the intercept as multiples of a, b, c say la, mb and nc.
3. Take reciprocals of l, m and n.
4. Clear fractions to get whole numbers h, k, l.
5. Miller indices of the plance are (h, k, l).

Interplanar Spacing in a Crystal System:

$$\frac{1}{(d_{hkl})^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2$$

where h, k, l are the miller indices

a, b, c are the dimensions of the cell.

for a cubic cell

$$a = b = c$$

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

X-Ray Crystallography:

A crystal lattice is considered to be made up of regular layers of or planes of atoms equal distance apart. Since the wavelength of X-rays is comparable to the interatomic distances, von Laue (1912) suggested that crystal can act as grating to X-rays. Thus when a beam of X-rays is allowed to fall on a crystal a large number of images of different intensities are formed. If the diffracted waves are in the same phase, they reinforce each other and a series of bright spots are produced on a photographic plate placed in their path. On the other hand, if the

diffracted waves are out of phase, dark spots are caused on the photographic plate. From the overall diffraction patterns produced by a crystal, we can arrive at the detailed information regarding the position of particles in the crystal. The study of crystal structure with the help of X-rays is called X-ray crystallography.

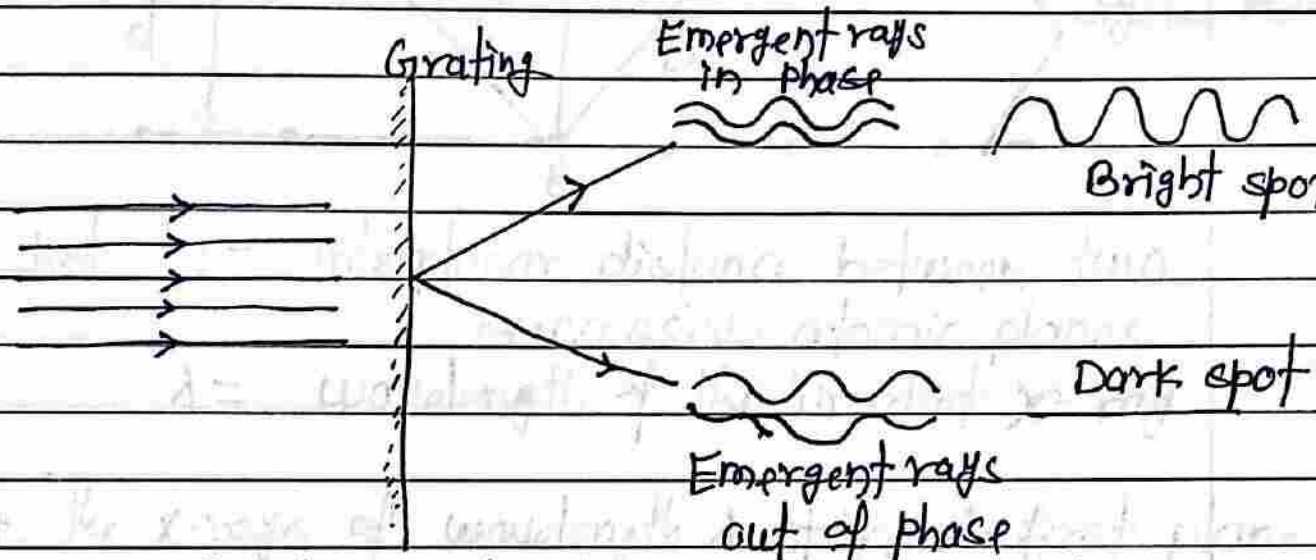


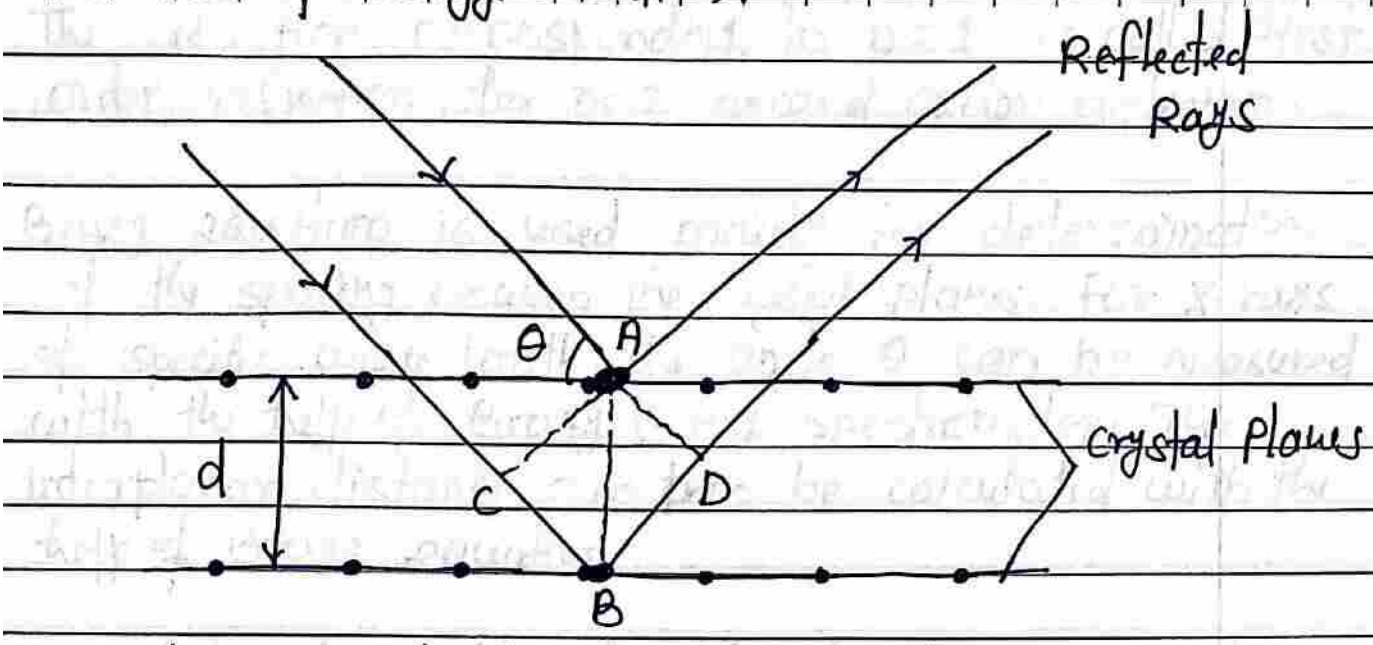
Fig: Diffraction pattern produced by crystals.

Bragg's Equation:

Equation which gives a relation between wavelength of the X-rays, the interplanar distance in a crystal and the angle of refledion is known as Bragg's equation. Bragg showed that.

1. The X-ray diffracted from atoms in crystal planes obey the laws of reflection.
2. The two rays reflected by successive planes will be in phase if the extra distance travelled by the second ray is an integral number of wavelengths.

Derivation of Bragg Equation:



Let d = interplanar distance between two successive atomic planes.

λ = wavelength of the incident X-ray

Let the X-rays of wavelength λ strike the first plane at an angle θ. Some of the rays will be reflected at the same angle. Some of the rays will penetrate and get reflected from the second plane. These rays will reinforce those reflected from the first plane if the extra distance travelled by them (CB + BD) is equal to integral number n of wavelengths. i.e.

$$n\lambda = CB + BD \quad \text{——— (1)}$$

Geometry shows that

$$CB = BD = AB\sin\theta \quad \text{——— (2)}$$

Put the value of CB and BD in equ (1).

$$n\lambda = AB\sin\theta + AB\sin\theta$$

$$\text{or } n\lambda = 2AB\sin\theta \quad \text{——— (3)}$$

$$AB = d$$

$$\therefore \boxed{n\lambda = 2d\sin\theta}$$ Bragg equation

The reflection corresponding to $n = 1$ is called first order reflection, for $n = 2$ second order reflection.

Bragg equation is used mainly for determination of the spacing between the crystal planes. For X-rays of specific wave length, the angle θ can be measured with the help of Bragg X-ray spectrometer. The interplanar distance can then be calculated with the help of Bragg equation.

2. Calculate the ratio of interplaner spacing (d_{hkl}) for a cubic system between the set of planes 111 and 222. Assumming the edge length of the unit cell is a.

Solution; for cubic system

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

$$\text{for } d_{111} = \frac{a}{\sqrt{1^2+1^2+1^2}} = \frac{a}{\sqrt{3}}$$

$$\text{for } d_{222} = \frac{a}{\sqrt{2^2+2^2+2^2}} = \frac{a}{\sqrt{12}} = \frac{a}{2\sqrt{3}}$$

Ration of interplanar spacing

$$\frac{d_{111}}{d_{222}} = \frac{a/\sqrt{3}}{a/2\sqrt{3}} = \frac{2}{1}$$

$$\therefore \boxed{d_{111} : d_{222} = 1 : 0.5}$$

Q. The density of $LiBH_4$ crystal is $0.668\ g/cm^3$ and the unit cell dimensions are $a = 6.81\ A^\circ$, $b = 4.43\ A^\circ$ and $c = 7.17\ A^\circ$. Determine whether the lattice is f.c.c or b.c.c. The molar mass of $LiBH_4 = 21.76\ g\ mol^{-1}$.

Solution: for cubic system

$$a = b = c$$

Hence it is not a cubic system.

Given $a = 6.81\ A^\circ$

$b = 4.43\ A^\circ$

$c = 7.17\ A^\circ$

$$\rho = \frac{nM}{N_A \cdot V}$$ where ρ = Theoretical density

n = No. of molecules or ions or atoms in the unit cell

M = Molar mass

V = Volume of the unit cell

for cubic system

$$\rho = \frac{n \cdot M}{N_A \cdot a^3}$$

But here $a \neq b \neq c$

$$\therefore \rho = \frac{n \cdot M}{N_A \times a \times b \times c}$$

$$\text{or } n = \frac{\rho \times a \times b \times c \times N_A}{M} \quad \text{---(i)}$$

$$n = \frac{0.668\ g/cm^3 \times 6.81 \times 10^{-8}\ cm \times 4.43 \times 10^{-8}\ cm \times 7.17 \times 10^{-8}\ cm \times 6.022 \times 10^{23}\ mol^{-1}}{21.76\ g\ mol^{-1}}$$

$$n = 3.99$$

So crystal is FCC.

Note

Primitive cubic unit cell $n = 1$
for bcc $n = 2$
for fcc $n = 4$

Q. When a certain crystal was studied by Bragg's method using X-rays of wavelength 0.299 nm, an X-ray reflection was observed at an angle of 23°20'. What is the corresponding interplanar spacing?

$\sin 23°20' = 0.396$

Solution:

$$n\lambda = 2d\sin\theta$$

$$d = \frac{n\lambda}{2\sin\theta} = \frac{n \times 0.299\ nm}{2 \times 0.396}$$

$$d = n \times 0.0453\ nm.$$

$$\boxed{d = 1 \times 0.0543\ nm}$$

Limitations of X-ray Diffraction / Bragg Law:

Bragg Law is unable to distinguish isoelectronic species i.e. if in any atom, ions or molecule the no. of $\bar{e}$ is same then diffraction pattern will also be same.

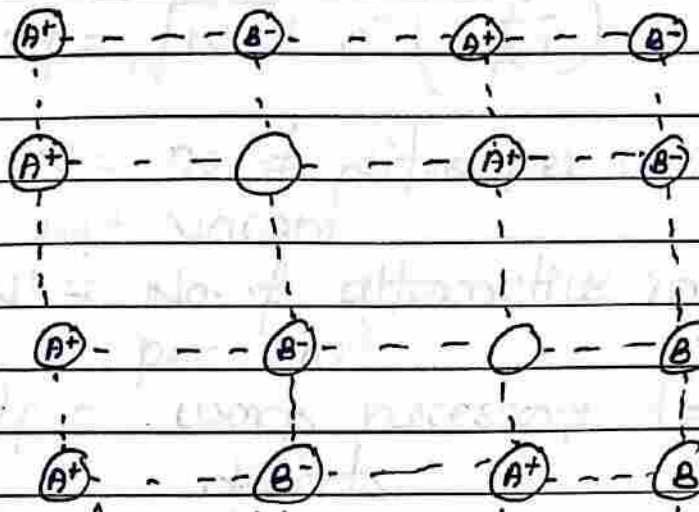
e.g. it is not possible to distinguish K^+ and Cl^- by X-ray diffraction this is because in both the ions no. of $\bar{e}$ns is same so diffraction pattern will also be same.

Defects in solid: Any deviation of the ideally perfect crystal from the periodic arrangement of its constituents is called defect or imperfection.

Two types of defects

- Point Defects
  - Occurs because of missing atoms, displaced atoms
  - Two types of Point defects
    - Schottky
      - Stoichiometric
      - Schottky
      - Frenkel
    - Frenkel
      - Non-Stoichiometric
      - Metal Excess.
        - F-centers
        - Interstitial ions & electrons.
      - Metal deficiency.
        - Positive ion absent
        - Extra interstial negative ions.
- Dislocation
  - Line Defects
  - → Occurs when periodicity of the atomic lattice arrangement is interupted in certain directions.
    - Edge
    - Screw.

Schottky Defects:



A pair of positive and negative ion is absent from the crystal lattice.

→ This defect occurs in highly ionic compounds where positive and negative ions are of a smaller size.

e.g. NaCl, CsCl, KCl & KBr.

The number of Schottky defects formed per cm^3 is given by

$$n_s = N e^{-W_s/2kT}$$

where n_s = no. of Schottky defects per cm^3

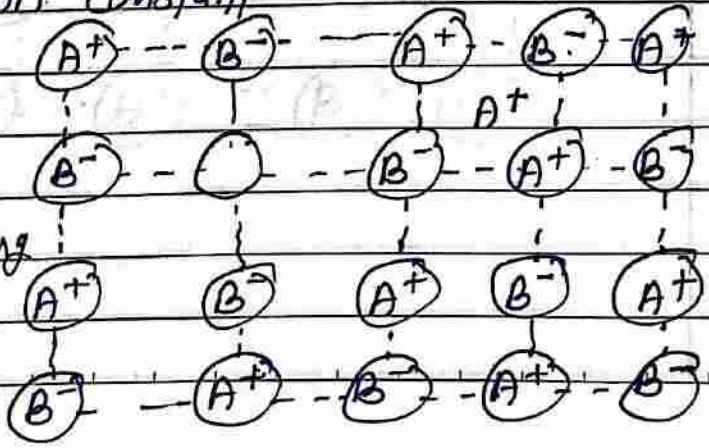
N = no. of sites per cm^3

T = absolute temprature

k = Boltzmann constant

Frenkel Defects:

A positive ion is absent from its lattice site leaving a hole and occupied in interstitial site.



The number of Frenkel defects formed per cm^3 (n_f) is given by

$$n_f = \sqrt{NN'}\, e^{-\left(\frac{W_f}{2kT}\right)}$$

where N = no. of sites per cm^3 that could be left vacant

N' = No. of alternative interstitial positions per cm^3

W_f = work necessary to form Frenkel defects

k = Boltzmann constant

T = absolute temprature.

e.g. ZnS, AgCl, AgBr, AgI.

intrinsic semiconduction.

Non-stoichiometric Defects:

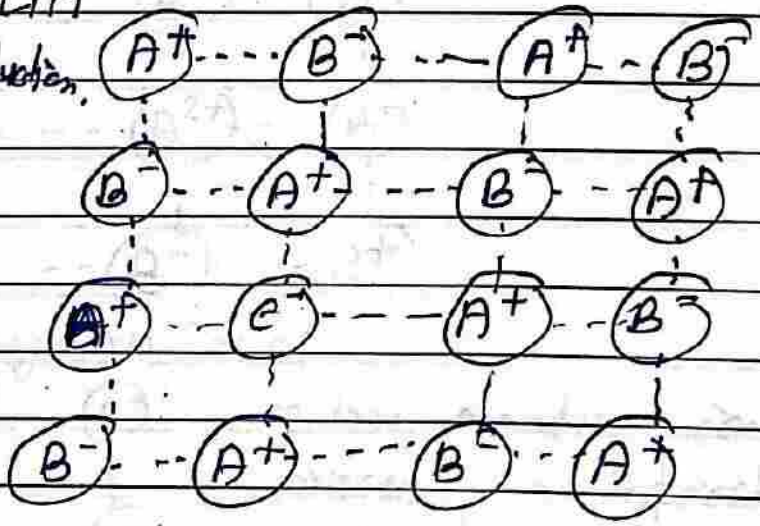
1. Metal Excess:

i) F-centres:

A negative ion is absent, leaving a hole which is occupied by $\bar{e}$.

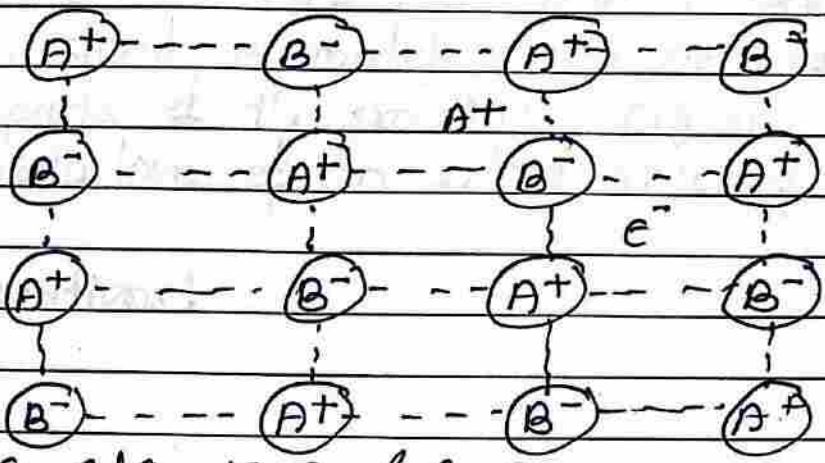
e.g. NaCl, KCl, LiH

n-type semiconduction.



i) Interstitial ions and electrons:

Extra metal ion and $\bar{e}$ occupied in interstitial position.



e.g. ZnO, CdO, Fe_2O_3 & Cr_2O_3.

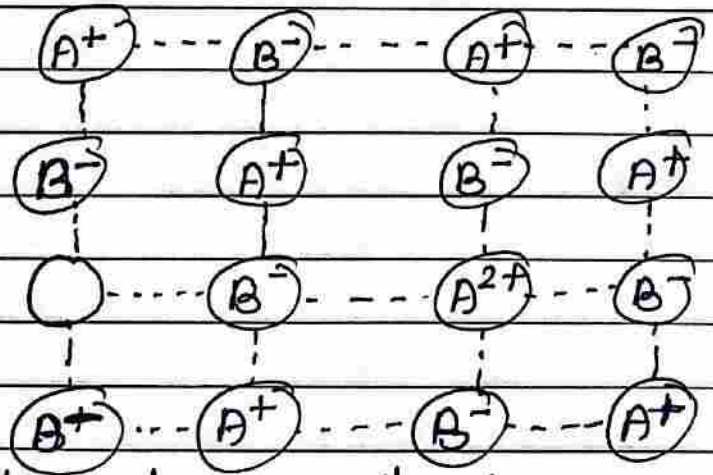
n-type semiconductors.

Metal Deficiency:

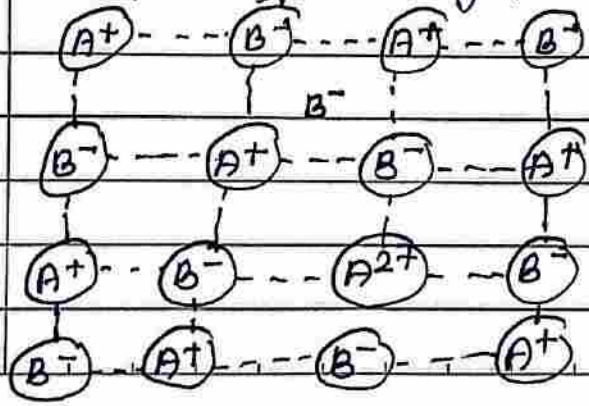
i) Positive Ion absent:

Positive ion absent and charge is balanced by adjacent metal having extra positive charge.

e.g.



ii) Extra Interstitial negative ions:



Extra negative ion is present in interstitial site and charge is neutralized by presence of dicationic metal ion.

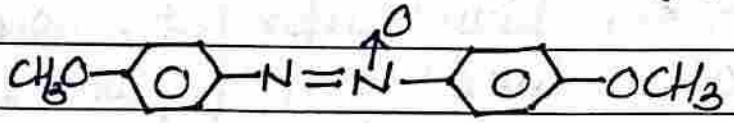
Line - Defects: Dislocations:

i) Edge-dislocations: Edge dislocation arises when there is slight mismatch in the orientation of adjacent parts of the growing crystal resulting in the introduction of an extra row of atoms.

Liquid Crystals: Some of the substance do not convert into liquid state directly. Instead they pass through an intermediate state called the liquid crystal state, often referred to as the liquid crystal. Thus the liquid crysted state is intermediate between the liquid state and the solid state.

Solid state ⟶ Liquid crystal ⟶ Liquid

e.g.



p-Azoxyanisole.

p-methoxy cinnamic acid.

The liquid crystals have a structure between that of a liquid and that of a crystalline solid. In a liquid the molecules have a random arrangement and they are able to move past each other. In a solid crystals the molecules have an ordered arrangement and are in fixed position. In a liquid crystals however molecules are arranged parallel to each other and can flow like a liquid. Thus the liquid crystals have the fluidity of a liquid and optical properties of solid crysteals. Therefore the term mesomorphic state is used for liquid crystals.

Types of Liquid Crystals:

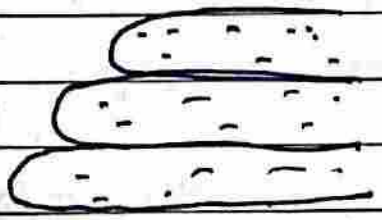
Three types

Smectic Liquid crystals

Nematic Liquid crystals.

Choesteric Liquid crystals.

1. Smectic Liquid Crystals:



They have limited mobility and do not flow like liquids
They flow in layers.
The flow of smectic liquid crystals is non-Newtonian while that of true liquid is newtonian.
→ Concept of viscosity is not applicable in case of smectic liquid crystals.
→ Smectic crystals also gives X-ray diffraction pattern like solids crystals but it is in one direction only.
e.g. ethyl p-azoxy benzoate, ethy p-ethoxy cinnamate, n-Octyl p-azoxy cinnamate. etc.

2. Nematic Liquid Crystals:
→ These liquid crystals exhibit nearly normal liquid behaviour i.e. their fluidity is much more than smectic liquid crystals.
→ Their flow behaviour is nearly Newtonian and thus concept of veiscosity is applicable for their flow. However the veiscosity of nematic liquid crystals is lower than that of normal liquid counterpart.
→ They are less truly anisotropic than smectic type.
→ They appear like thread like when viewed in plane polarised like. e.g. p-azoxy anisole, p-methoxy cinnamic acid etc.

Chloesteric Liquid Crystals:

Liquid crystals having some smectic and some nematic liquid crystal characters are called Cholesteric liquid crystals.

The mixed behaviour is exhibited by some optically active compounds like l- Cholesteryl esters.

Glasses:

Glass is an amorphous solid material which is under the category of non-crystalline solids.

Glasses are typically brittle and optically transparent material.